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ORIGINAL ARTICLE

Miswak mediated green synthesized palladium nanoparticles as effective catalysts for the Suzuki coupling reactions in aqueous media

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Abstract Green and eco-friendly synthesis of palladium nanoparticles NPs is carried out under facile and eco-friendly conditions using an aqueous solution of *Salvadora persica* L. (SP) root extract (RE) as a bioreductant, which is commonly known as Miswak. The as-synthesized Pd NPs were characterized using various spectroscopic and microscopic techniques, including, UV–Vis spectroscopy, FT-IR spectroscopy, XRD, ICP-MS and TEM. Detailed investigations of the Pd NPs have confirmed that the polyphenolic phytochemicals present in the RE of Miswak not only act as a bioreductant by facilitating the reduction and growth of Pd NPs, but they also functionalize the surface of Pd NPs and stabilized them in various solvents. Furthermore, the catalytic activity of the green synthesized Pd NPs was also tested toward the Suzuki coupling reactions of various aryl halides in aqueous media. The as-prepared Pd NPs exhibited superior catalytic activity and reusability for the Suzuki coupling reaction in aqueous and aerobic conditions. The kinetics of the reaction studied by GC revealed that the conversion of various aryl halides to biphenyl takes place in a short time.

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1. Introduction

Nanotechnology has emerged as the most promising field of multidisciplinary science [1,2]. Due to their small size, nanoparticles (NPs) possess excellent physicochemical properties, which are completely different from their bulk counterparts [3]. These properties have been extensively exploited in several technological fields, including catalysis [4,5]. Among various nanomaterials, metallic NPs have a significant importance in human life

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[6]. Therefore, metallic NPs, including, Ag, Au, Pd, Pt, etc. have been extensively studied for several decades [2,7]. A number of studies have been reported involving the synthesis, characterization and applications of metallic NPs with particular focus on the size and morphology of the NPs [8–10]. So far, several methods have been applied to prepare metallic NPs, and these methods are mainly classified into two different categories that include physical and chemical methods. The preparation methods are usually selected according to the feasibility and accessibility of the protocols to achieve the targeted applications [11,12]. The physical methods, such as, ball milling, laser ablation, flame pyrolysis, etc. often require expensive instruments, high temperature and pressure.

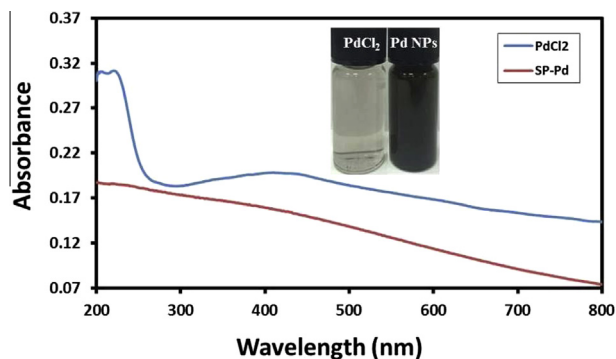


Figure 1 Ultraviolet–visible (UV–Vis) absorption spectra of the corresponding solution depicting the reduction of PdCl_2 to metallic Pd.

Chemical methods are largely used for the preparation of metallic NPs, which are more facile and less expensive, when compared to the physical methods [8]. The chemical synthesis of metallic NPs involve the concepts of wet chemistry, where the reduction/decomposition of metal complexes is carried out in solutions using various chemical reductants, such as sodium borohydride, hydrazine or at elevated temperature [13,14]. Although, the chemical methods have been extensively used for the preparation of metallic NPs, the reactants, reductants, stabilizers and various organic solvents used in these methods are toxic and potentially hazardous to the environment [15,16]. Due to the growing environmental concerns,

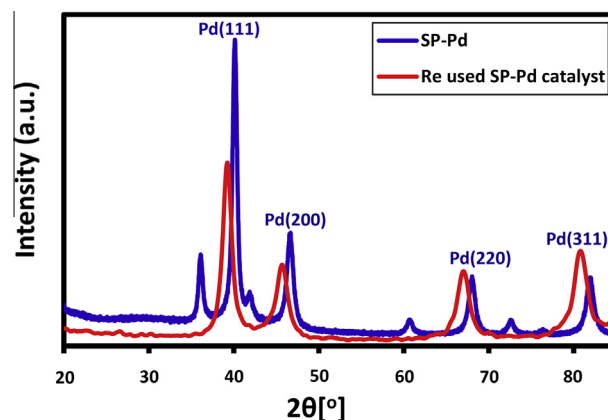


Figure 2 XRD diffraction pattern of as-synthesized palladium nanoparticles (Pd NPs).

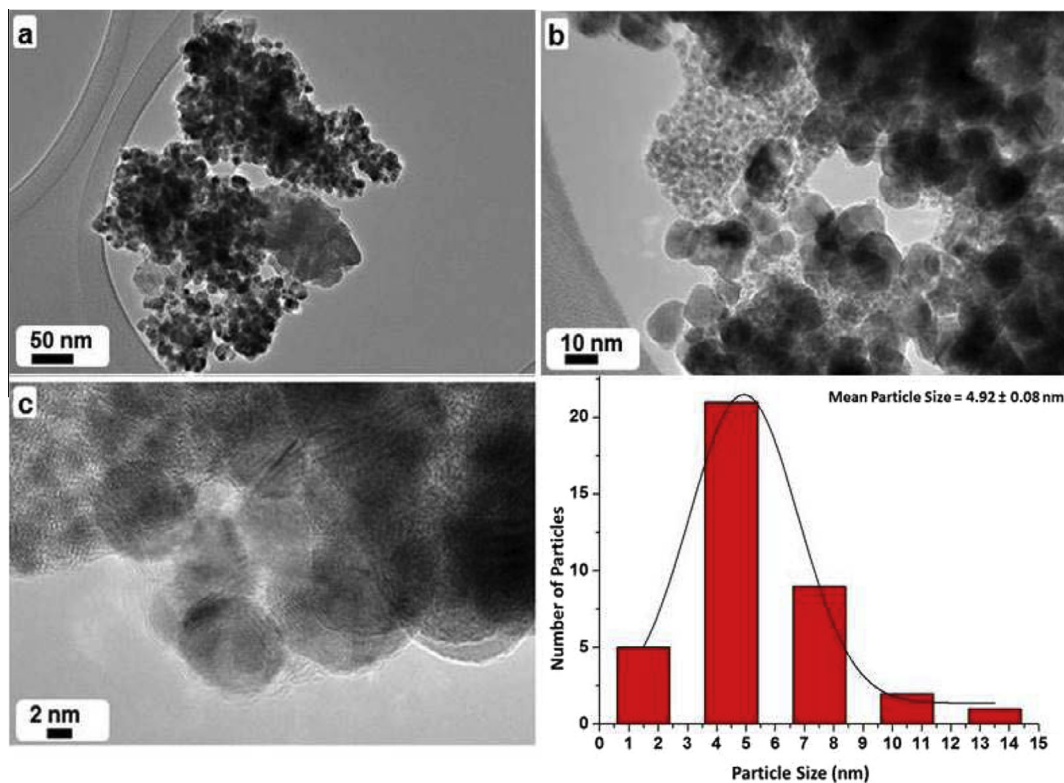


Figure 3 Transmission electron microscope (TEM) and high resolution (HRTEM) images of the Pd NPs (a) overview, (b) and (c) magnified HRTEM image (d) particle size distribution graph.

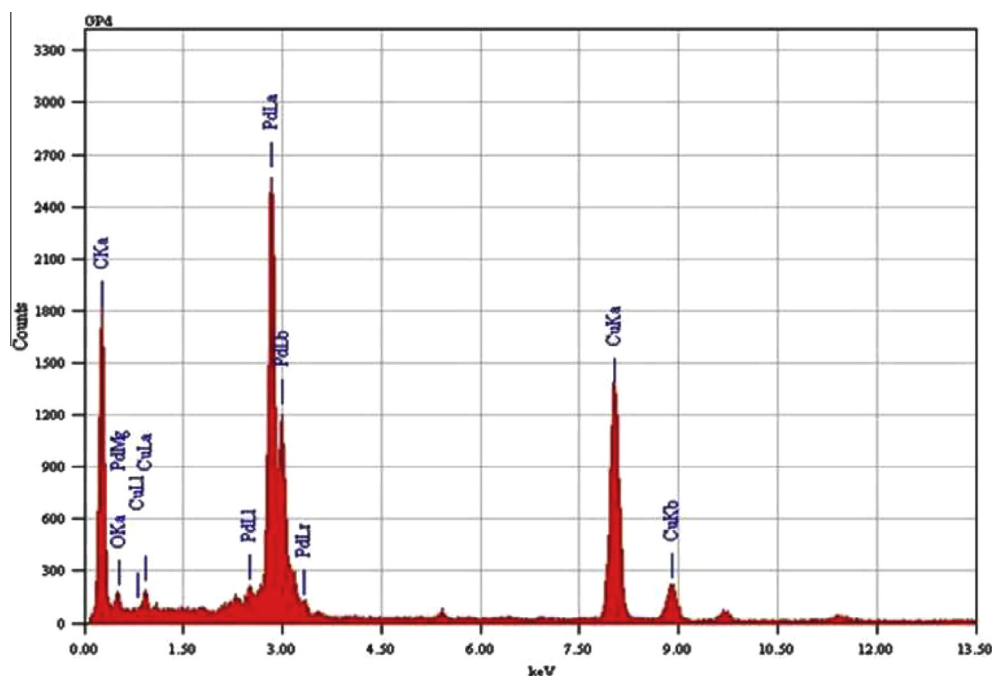


Figure 4 Energy dispersive X-ray spectrum (EDX) of as-synthesized Pd NPs confirming the composition of product.

Table 1 Time dependent conversion efficiency of the Suzuki reaction of chlorobenzene, bromobenzene and iodo benzene.

R. No.	Reactants	Products	Time taken (min)	Conversion (%)
1			5	100
2			8	100
3			25	80

the development of more alternative facile green approaches for the preparation of NPs under ambient conditions using non-toxic reagents and solvents is highly desirable [17,18].

Currently, eco-friendly syntheses of metallic NPs have attracted significant attention of the scientific community. Various methods have been used to prepare metallic NPs under physiological and eco-friendly conditions, which include electrochemical, microwave, sonochemical, supercritical liquids, ionic liquids, etc. [19–21]. Apart from this, several other methods have also been used that involve various green materials as bio-reductants to produce metallic NPs under aqueous conditions [22]. For instance, several marine organisms, microorganisms, extracts of biomolecules, plants and proteins were also applied for the green synthesis of metallic NPs [23,24]. However, among these materials the plant extracts (PE) have recently gained considerable interest of the scientific community. Since the plant extracts are easy to use, less expensive

and do not require sophisticated laboratory facilities and toxic chemicals and solvents, therefore they easily facilitate the large scale biosynthesis of metallic NPs [25–28].

Apart from various applications, metallic NPs have been extensively exploited in the field of catalysis [29,30]. Among various metallic NPs, palladium (Pd) has played a critical role as catalyst, and has been widely applied both as heterogeneous and homogeneous catalysts in several organic reactions [31,32]. So far several catalytic reactions were carried out using Pd NPs as catalysts, including carbon–carbon coupling reactions, such as Suzuki coupling reactions and so on [33]. However, in most cases Pd nanocatalysts were either prepared by chemical methods or various other methods which usually involve different toxic chemicals, polymers, metal organic frameworks, etc. [34]. Only few studies are reported using the PE, where the Pd NPs were synthesized using PE and used as catalysts under aqueous conditions [35].

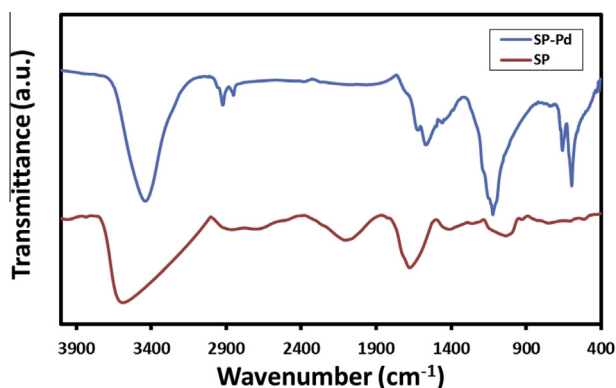


Figure 5 Fourier transform-infrared spectra of pure green synthesized palladium nanoparticles (Pd NPs) (blue line) and *S. persica* L. RE (red line).

Usually, coupling reactions, including Suzuki reactions are carried out under inert conditions using a mixture of an organic solvent and an aqueous inorganic base [36]. However, carrying these reactions under aerobic conditions is highly desirable. Therefore, considerable studies have been conducted in this regard, where different types of the Suzuki reactions were performed under aqueous conditions; however, these reactions usually require activation by phosphine ligands [37]. Nevertheless, certain studies have also been conducted where the methods for the Suzuki reactions that do not require pre-activation are reported [38]. For instance, in a recent study, *Hippophae rhamnoides* Linn. leaf extract was used to prepare crystalline Pd NPs, which were used as catalysts for the Suzuki–Miyaura coupling reaction under aqueous conditions [39]. Similarly, in our previous study, we demonstrated a facile method for the preparation of small size, crystalline Pd NPs by an aqueous solution of *Pulicaria glutinosa* PE as a bioreductant. The as-synthesized Pd NPs were utilized as a catalyst for the Suzuki coupling reaction under aqueous and aerobic conditions.

In this study, we have used *Salvadora persica* L. (SP) extract as a bioreductant, which is commonly known as Miswak. The large number of polyphenolic and flavonoidic phytochemicals present in the Miswak extract considerably enhance its reducing ability and also act as stabilizing agents. The reducing and stabilizing ability of the Miswak has already been tested for the reduction of graphene oxide [40].

Herein, we describe an ecofriendly method for the preparation of Pd NPs (SP-Pd) under aqueous conditions using *S. persica* L. root extract (SP) as bioreductant. The SP-Pd was characterized using different analytical and microscopic methods such as, Fourier transform infrared spectroscopy (FT-IR), ultraviolet–visible (UV–Vis) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). Furthermore, the as-synthesized Pd NPs were also utilized as catalysts for Suzuki coupling reactions, which were carried out under aqueous conditions. During this study, we followed a method, where the Suzuki reaction was performed without any pre-activation [41]. Subsequently, a detailed kinetic investigation of the catalytic coupling reaction was also carried out, and

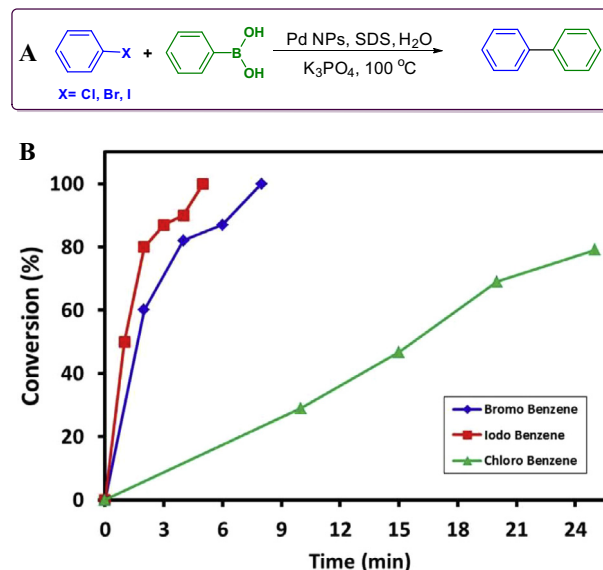


Figure 6 (A) Schematic representation of the Suzuki reaction of chlorobenzene, bromobenzene and iodobenzene with phenylboronic acid under aqueous conditions. (B) Time dependent conversion efficiency of the Suzuki reaction of chlorobenzene, bromobenzene and iodo benzene with phenylboronic acid under aqueous and aerobic conditions determined by GC analysis.

the final product was characterized using gas chromatography–mass spectrometry (GC–MS).

2. Experimental

2.1. Materials and methods

S. persica L. roots were purchased from Batha, a local herbal market in Riyadh, Kingdom of Saudi Arabia (KSA). These roots are commonly grown in the southern region of KSA, including Jizan. The identification of the plant material was performed by a plant taxonomist from the King Saud University, Riyadh, KSA. A voucher specimen was retained in our laboratory with the voucher specimen number KSUHZK-302. PdCl₂ (99.9%), Bromobenzene (97%), chlorobenzene (97%), sodium lauryl sulfate (98%), benzenboronic acid (97%), K₃PO₄ (98%), ethyl acetate (~88%) and other organic solvents were procured from Sigma–Aldrich (St Louis, MO, USA) and used without further purifications.

2.2. Preparation of *S. persica* L. root extract

Fresh roots of *S. persica* L., were cut into small pieces and soaked in 300 mL of deionized water, the mixture was allowed to reflux for about four hours. Subsequently, the resultant solution obtained after the reflux was filtered using a Buchner funnel and dried at 50 °C under vacuum in a rotary evaporator to obtain a dark brownish gummy extract (30.0 g), which was collected and stored at 0–4 °C for further use.

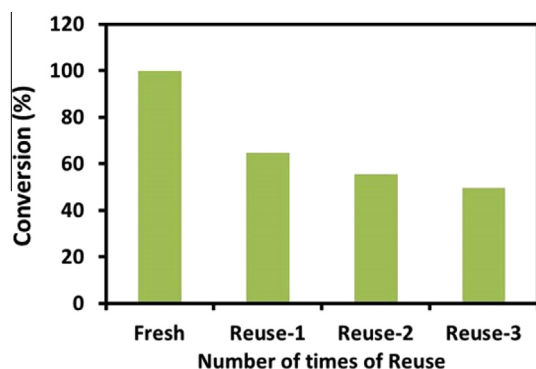


Figure 7 Graphical representation of conversion product obtained by the reuse of catalyst for the catalytic conversion of bromobenzene.

2.3. Preparation of Pd NPs

Initially, 0.5 mM PdCl_2 (88.66 mg) was dissolved in 50 mL of water in 100 mL round bottomed flask. To this solution, 2.5 mL of *S. persica* L. gummy RE was added. Subsequently, the flask was equipped with a magnetic stir bar and a cooling condenser, and the mixture was stirred for 2 h at 90 °C. Upon heating, the color of the solution gradually changed from light yellow to dark brown, however, after two hours no further color change was detected, which indicated toward the completion of the reaction. After this, the mixture was allowed to cool down and centrifuged at 9000 rpm. Finally, the precipitate was collected and washed thrice with deionized water to obtain a black powder which was kept overnight in an oven at 80 °C.

2.4. Pd NPs catalyzed Suzuki reaction

A mixture of benzenboronic acid (146 mg, 1.2 mmol), sodium lauryl sulfate (144 mg, 0.5 mmol), K_3PO_4 (399 mg), and 20 mL of deionized water was taken in a flask (100 mL). To this mixture, 1 mmol of bromobenzene (157.01 mg) or 1 mmol of chlorobenzene (112.56 mg) was added while stirring. Subsequently, 5 mol% of as-synthesized Pd NPs (5.32 mg) was added to the mixture. Thereafter, the mixture was stirred for two hours in an oil bath at 100 °C. After this time the mixture was extracted three times using 20 mL of ethyl acetate each time. The organic extracts were combined and dried over anhydrous Na_2SO_4 . Finally, the mixture was collected and analyzed via gas chromatography (GC). This product was further confirmed as biphenyl using mass spectroscopy (EIMS m/z 154 (M^+)) and solution NMR (^1H and ^{13}C). ^1H NMR δ 7.20–7.24 (m, 6H, edge protons of phenyl ring), 8.22 (d, 4H, C–CH, next to ipso, $J = 8.3$ Hz); ^{13}C NMR δ 141.1 (2C, C–C, ipso), 128.3 (4C, CH–CH), 126.9 (2C, CH–CH, edge carbons), 127.4 (4C, C–CH, next to ipso).

In order to reuse the Pd NPs as catalyst in the same Suzuki reaction, the Pd NPs were collected after the reaction via centrifugation. The collected precipitate is washed several times to remove any organic moieties present on the surface of the NPs. Subsequently, the purified NPs were used for further catalytic cycles.

2.5. Characterization

The as-synthesized Pd NPs and the product obtained from the Suzuki reactions were characterized by UV–Vis spectroscopy (Perkin Elmer lambda 35 (Waltham, MA, USA)), high-resolution transmission electron microscopy (HRTEM) (JEM 1101 (JEOL, Tokyo, Japan)), FT-IR spectroscopy (Perkin Elmer 1000 FT-IR spectrometer), energy dispersive X-ray spectroscopy (EDX) (JEM 1101 (JEOL, Tokyo, Japan)), mass spectroscopy (Agilent spectrometer (single quadrupole) MSD-5975C detector, Agilent Technologies Inc., USA, MS was acquired in EI mode (scan range m/z 45–600, ionization energy 70 eV)), nuclear magnetic resonance spectroscopy (NMR) (JEOL ECP-400 spectrometer) and gas chromatography (GC) (GC 7890A, Agilent Technologies Inc., equipped with a flame ionization detector (FID) and a 19019S-001 HP-PONA column). All the NMR samples were prepared in CDCl_3 with TMS as an internal standard. The XRD analysis of the as-prepared Pd nanocatalysts were carried out using a D2 Phaser X-ray diffractometer (Bruker, Germany), $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The ICP-MS analysis was carried out by Perkin Elmer Sciex Elan inductively coupled plasma mass spectrometer model 9000 (Canada).

3. Results and discussions

The green synthesis of Pd NPs was performed under facile conditions by the reduction of an aqueous solution of PdCl_2 using the *S. persica* L. (Miswak) root extract (RE) as a reducing agent at 90 °C. During synthesis, the additional use of any other hazardous or harmful chemical reducing agent was not required, as the Miswak RE effectively reduces PdCl_2 solution to produce Pd NPs. This was clearly indicated by the gradual change in the color of the aqueous solution of PdCl_2 from light brown to dark brown upon addition of the Miswak RE (cf. Fig. 1).

The synthesis of Pd NPs was initially confirmed by UV–Vis spectroscopy. For this purpose, the UV–Vis spectra of aqueous solution of pure PdCl_2 and Pd NPs (formed at 90 °C) was measured, which is given in Fig. 1b. All the samples for the UV measurements were prepared as reported in our previous study [42]. The UV spectrum of PdCl_2 solution consists of an absorption band at 415 nm, which is the characteristic band of PdCl_2 and appear by the absorption of Pd ions (Pd(II)). However, after reduction, the band at 415 nm completely disappeared in the spectrum of Pd NPs, whereas a broad and continuous absorption band appeared which clearly indicated the reduction of Pd(II) ions and the formation of Pd(0) NPs.

To confirm the crystallinity of the as-prepared Pd NPs, the sample was characterized by powder XRD analysis. The XRD pattern of Pd NPs exhibited five distinct reflections at 40.02° (111), 46.49° (200), 68.05° (220), 81.74° (311) and 86.24° (222) as shown in Fig. 2. These are the characteristic reflections of face centered cubic (*fcc*) structure of Pd (JCPDS: 87-0641, space group: $\text{Fm}\bar{3}\text{m}$ (225)) [43]. Among all the reflections, the reflection at 40.02° (111) is the most intense compared to other reflections, which may indicate the preferred direction for the growth of the nanocrystals [44]. Based on the half width of the most intense reflection (40.02°) the average crystallite size (~ 10 nm) of the Pd NPs was calculated

using the Scherer equation [45]. Notably, apart from the reflections belonging to the Pd NPs, some other additional reflections are also found in the diffraction pattern of Pd NPs obtained using *S. persica* L. (Miswak) RE (cf. Fig. 2). These additional reflections possibly belong to some of the residual moieties of the RE. A comparison of XRD patterns between the as-synthesized palladium nanoparticles (Pd NPs) and reused catalyst (cf. Fig. 2) was carried out and from this it can be observed that there is no change in crystalline phases of the nanoparticles. However, the additional reflections assigned to the residual moieties of the RE are missing from the reused catalyst. This could be due to the dissolution of the phytomolecules that were capping the Pd NPs nanoparticles.

The as-synthesized Pd NPs were further characterized using transmission electron microscopy (TEM) to investigate the morphology and size of the Pd NPs. The overview of the TEM images of Pd NPs is shown in Fig. 3, which depicts the size distribution and morphology of the as-synthesized Pd NPs. The NPs are spherical in shape with a diameter of ~ 2.2 – 15 nm. Clearly, highly crystalline Pd NPs with a narrow size distribution were observed, which is attributed to the presence of phytomolecules as stabilizing agents. This is also confirmed by the close investigation of TEM images of Pd NPs which revealed the existence of an organic layer (light contrast) on the surface of the NPs.

Furthermore, the elemental composition of the as-prepared NPs was also evaluated via EDX is shown in Fig. 4, which clearly indicates the presence of Pd. However, apart from Pd, carbon and oxygen were also present in considerable amount in the EDX spectrum, which clearly suggest the presence of residual molecules of the RE as stabilizing agents on the surfaces of the NPs.

Furthermore, the dual role of the RE, both as bioreductant and stabilizing agent was confirmed by FT-IR spectroscopy as reported in our earlier studies [46]. For this purpose, IR spectra of both as-prepared Pd NPs as well as the RE were measured (cf. Fig. 5). The comparison of the FT-IR spectra of both as-prepared Pd NPs and pristine RE clearly indicates the presence of the phytomolecules of the RE on the surface of Pd NPs. The spectrum of the RE consists an absorption peaks at 3627 cm^{-1} for hydroxyl groups, which points to the presence of various oxygen containing functional groups, such as carbonyl, carboxylic, epoxy and hydroxyl groups. The peak at $\sim 2933\text{ cm}^{-1}$ points toward the presence of C–H, $\sim 2132\text{ cm}^{-1}$ (for C=O stretching), $\sim 1698\text{ cm}^{-1}$ (for C=C stretching), $\sim 1000\text{ cm}^{-1}$ (for C–O stretching). Most of the absorption bands of the *S. persica* L. pure RE also appear in the FT-IR spectrum of purified Pd NPs, either at same position or with slight shifts, such as the bands at ~ 3488 , ~ 2960 , ~ 1626 , and $\sim 1156\text{ cm}^{-1}$. The appearance of these bands in IR spectrum of Pd NPs, clearly suggests that the phytomolecules of *S. persica* L. RE not only act as bioreductant, but also function as capping ligands on the surface of the Pd NPs.

The green synthesized Pd NPs were used as catalysts in the Suzuki Miyaura coupling reactions. The catalytic activity of the as-prepared Pd NPs was evaluated in the Suzuki reaction of various aryl halides, including, chloro, bromo and iodobenzene with benzenboronic acid. The Pd NPs obtained from the *S. persica* L. RE catalyzed the reactions of chlorobenzene or bromobenzene with benzenboronic acid in water containing

sodium lauryl sulfate and K_3PO_4 under aerobic conditions to obtain biphenyl (cf. Fig. 6A). Furthermore, detailed kinetic studies of the Suzuki reaction was also performed, which was carried out using 5 mol% of the Pd NPs prepared using *S. persica* L. RE as a catalyst.

The samples for kinetic study of the reaction were collected every minute and quenched immediately. The collected samples were analyzed using gas chromatography (GC–FID) equipped with a capillary column (HP-PONA). The temperature profile for GC was as follows. The starting column temperature was 120°C , which was increased to 180°C at a ramp rate of $10^\circ\text{C min}^{-1}$ and maintained at this temperature for 5 min. The GC results (see Table 1) clearly indicate that different derivatives of benzene gave the coupled product at different reaction times, it took 5 min for the iodobenzene derivative to give 100% conversion product while it took 8 min and 25 min for the bromobenzene, chlorobenzene derivatives respectively, as shown in the graphical representation of the kinetics of the reaction in (Fig. 6B). It can be noticed from the graph that $\sim 25\%$ of the reaction was already completed within ~ 2 min of the beginning of the reaction with the iodobenzene and bromobenzene derivatives. After this induction period, a 100% conversion product was obtained for iodobenzene and bromobenzene derivative within minutes, but in the case of chlorobenzene, a max of 80% conversion product was obtained at 25 min, which was not continued further. In order to further confirm the formation of coupled product obtained from the reaction, the as-obtained mixture was subjected to crystallization using ethanol. The resulting crystallized material was confirmed by mass spectroscopy, which revealed that the obtained product is biphenyl (EIMS m/z 154 (M^+)).

Furthermore, an attempt was made to reuse the as-prepared green synthesized Pd nanocatalyst, which was found to be successful and displayed a decline in catalytic performance when used up to three cycles of reuse. A graphical representation is given in Fig. 7. A leaching of the Pd into the reaction mixture could be the probable reason for the decline in the catalytic activity and in order to ascertain this decline in catalytic performance, the product obtained from the 3rd reuse of catalyst was subjected to ICP-MS. The studies revealed that there is an appreciable amount of Pd nanoparticles leached into the reaction mixture, which was detected along with the product.

4. Conclusions

Herein, green synthesis of Pd NPs is demonstrated using an eco-friendly material i.e., *S. persica* L. root extract (Miswak), which was used both as a bioreductant and stabilizer. During this synthesis, highly crystalline, spherical-shaped Pd NPs were obtained without using any harmful chemical reagents as reducing or capping agents. Detailed investigations have revealed that the polyphenolic phytomolecules, which are present in the RE not only facilitated the reduction of PdCl_2 , but they also helped to functionalize the surface of Pd NPs by acting as stabilizers. Furthermore, the as-synthesized Pd NPs demonstrated excellent catalytic activity toward various Suzuki coupling reactions, which were carried out in water under facile and aerobic conditions. The kinetic studies of the reactions, which were monitored by GC revealed that the

conversions of various phenyl halides to biphenyl occur in a very short time. Therefore, the eco-friendly method presented here for the preparation of metallic NPs may provide a better alternative for a large-scale production of different functional nanomaterials for various applications, including catalysis. The catalytic activity results of bromobenzene are comparable with our earlier studies [44] using a different plant extract (*P. glutinosa*). This may be because the morphology and size of palladium nanoparticles are similar in both the cases. It may be concluded from these results that controlled synthesis of palladium nanoparticles can be achieved using different plant extracts resulting in similar size and morphology. Furthermore, it can yield similar catalytic performance for Suzuki coupling reactions.

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